Effects of heat treatment on diffusion of Cu atoms into CdTe single crystals

Y. L. Soo, S. Huang, S. Kim, G. Kioseoglou, and Y. H. Kao[a)]
Department of Physics, State University of New York at Buffalo, Amherst, New York 14260

A. D. Compaan and D. Grecu
Department of Physics and Astronomy, University of Toledo, Toledo, Ohio 43606

D. Albin
National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401

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Angular dependence of x-ray fluorescence and x-ray absorption fine structure techniques have been used to study the diffusion of Cu atoms into the photovoltaic material CdTe. Depth profile, effective valency, and local structure of Cu atoms in a Cu-doped single crystal of CdTe were investigated before and after a second heat treatment. Enhanced Cu diffusion into the CdTe single crystal was observed as a result of heating at a moderate temperature around 200 °C, resulting in a redistribution of the Cu impurities through a broader depth profile. Some of the Cu atoms are believed either to form small complexes with Te or occupy interstitial sites in the host but accompanied by a large local lattice distortion while others substitute for Cd on the cation sites. The results thus demonstrate that these nondestructive x-ray characterization methods are useful for probing microstructural changes in CdTe photovoltaic materials/devices in which some Cu-containing compounds are used as back contacts. © *2000 American Institute of Physics.* [S0003-6951(00)03625-1]

Heterojunctions utilizing the direct gap semiconductor CdTe have been known for many years as important materials used in high-efficiency photovoltaic devices.[1,2] Many outstanding physical properties such as the sensitive short-wavelength response, structural stability, and high radiation tolerance, make this class of material a promising contender for large-scale development of the next-generation solar cells. However, the effects of heat treatment or prolonged light soaking on the stability of these devices are not well understood. It has been suggested that some observed degradation problems of the CdTe solar cells could probably be caused by the diffusion of Cu atoms from the back contact into CdTe when the solar cells are subjected to prolonged light soaking or heating.[3] Our recent studies of CdTe/CdS heterojunctions have also shown that heat treatment even at moderate temperatures can indeed lead to significant variations in the composition and interfacial microstructures.[4–7] It is plausible that changes of the microstructures in the layered material, or the incorporation of foreign atoms (such as Cu from the back contact), could in principle give rise to unwanted scattering of charge carriers as well as changes in the electronic structure in the solar cell, thereby leading to a lowered light-conversion efficiency. At the same time, Cu diffusion towards the CdS/CdTe heterojunction may be beneficial if Cu-related defects enhance *p*-type behavior in the CdTe near that interface. In view of the importance of the effects of Cu diffusion into CdTe, physical understanding of the possible location of the Cu impurities and the associated changes in its local environment would seem highly desirable.

In the present work, Cu impurities have been introduced into single crystals of CdTe and the changes in the Cu depth profile as well as local structures around Cu atoms after a second heat treatment have been investigated by using the techniques of angular dependence of x-ray fluorescence (ADXRF) and x-ray absorption fine structure (XAFS). These nondestructive methods allow the possibility of probing the distribution of Cu impurity atoms in the direction normal to the sample surface and the local environment as well as effective valency of Cu atoms in CdTe; all are useful for probing the mechanisms related to the efficiency changes caused by thermal, electrical, or illumination-induced stress. The microstructural information obtained with single crystals of CdTe is free from the influence of grain boundaries as opposed to the polycrystalline CdTe films used in practical devices. For the present study of the main effects of Cu diffusion into CdTe, our choice of a CdTe single crystal thus eliminates the possible complications which could arise from the presence of grain boundaries. Nevertheless, the data obtained in this study will serve as a useful reference which will eventually be needed for investigating the grain boundary effects when polycrystalline CdTe layers are used in the photovoltaic devices.

A Cu-doped CdTe single crystal sample, 1.0 mm thick, was prepared by evaporating 10 nm of Cu at room temperature followed by diffusion for 1 h at 200 °C in air. The remaining metallic and oxidized Cu on the surface was removed by a 15 s dip in 0.5% Br in methanol. The ADXRF and XAFS measurements were performed at beamline X3B1 of the National Synchrotron Light Source at Brookhaven National Laboratory. For a comparison of the microstructures around Cu atoms before and after heat treatment, all the x-ray measurements were repeated after the Cu-doped CdTe single crystals underwent a second heat treatment at 200 °C for 1 h.

For the ADXRF measurements, the intensity of Cu $K\alpha$

a)Electronic mail: yhk@acsu.buffalo.edu

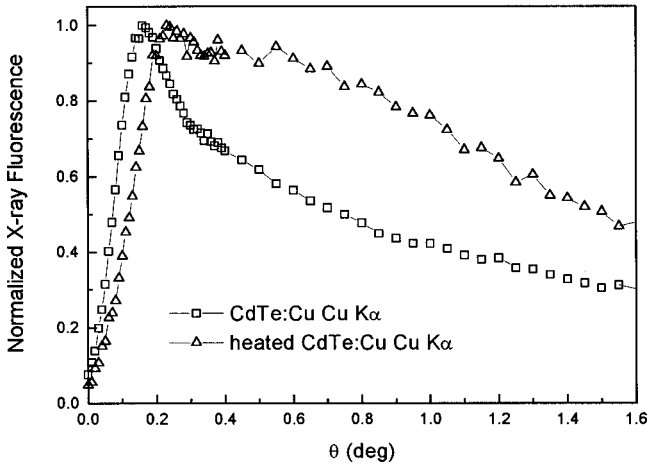

FIG. 1. ADXRF data for Cu $K\alpha$ emission vs θ normalized to the respective maximum value of each plot.

FY of the Cu-doped CdTe can be expressed as[8,9]

$$I_{\mathrm{FY}} \propto \int dz \left(-\frac{dS_z(z)}{dz} \right) \Phi(z), \tag{1}$$

where S_z is the z component (perpendicular to the interfaces) of the Poynting vector, and $\Phi(z)$ is the density profile of the Cu atoms in the z direction. As θ changes, information about the Cu depth profile can be obtained. The normalized Cu $K\alpha$ ADXRF results for the Cu-doped CdTe before and after the second heat treatment are shown in Fig. 1.

The Cu K-edge XAFS experiments were performed before and after heating. Detailed experimental and data analysis procedures were the same as described in our previous experiments.[10–13] The standard XAFS results are shown in Fig. 2. The local structural parameters determined by curve fitting of EXAFS functions are listed in Table I.

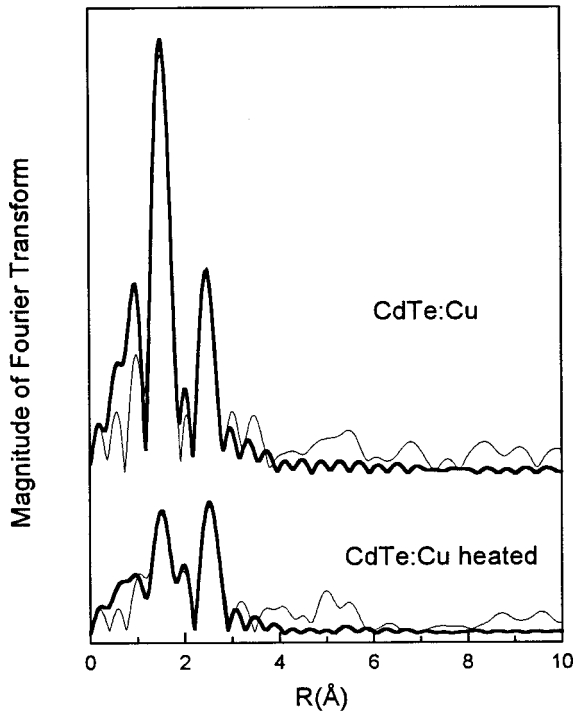

FIG. 2. Fourier transform of Cu K-edge EXAFS χ functions. Fine lines: experimental; course lines: theoretical.

As shown in Fig. 1, the normalized angular dependence of integrated Cu $K\alpha$ FY intensity for the sample prior to second heating shows a peak around the grazing angle $\theta = 0.16°$, followed by a rapid decrease in higher angles. As discussed in a previous work on ADXRF,[14] this feature offers a clear indication that the depth profile of Cu in this sample is distinct from that of a bulk material with a uniform Cu distribution (where the Cu $K\alpha$ intensity should increase monotonically with θ). In fact, by a direct comparison with model calculations,[14] this peak represents a feature which is characteristic of the fluorescent Cu impurity atoms being distributed mostly in a thin layer near the top of the CdTe host. After the second heating, this peak has shifted to a higher angle around 0.24° with a much slower decrease at higher angles as compared to the data obtained before heating. For a rough estimate of the depth distribution of Cu impurities, the raw ADXRF data as well as the normalized results (Fig. 1) are compared with a calculation of the penetration depth of x rays into CdTe at 9.02 keV as a function of θ. Around the position of the two peaks in Fig. 1, the estimated x-ray penetration depth is about 2–3 nm, and it increases to 200 nm at θ near 1.5°. This estimate indicates that before the second heating the depth distribution of Cu atoms is mostly centered around a shallow layer about several nanometers beneath the sample surface, but with some traces of pure Cu remained on the top surface. After heating, most Cu atoms move to a larger distance about 50–100 nm under the surface, with a long tail distribution probably extending up to several hundred nm deep into the CdTe crystal. In view of the overall changes in ADXRF, it is clear that the Cu impurities have been largely redistributed in the CdTe crystal as a result of second heating at 200 °C for 1 h. The shift of the ADXRF peak towards a higher angle indicates that most of the Cu atoms have been driven deeper into the CdTe crystal and it therefore requires further penetration of the incident x rays at higher grazing incidence angles in order to excite the Cu $K\alpha$ fluorescence from these Cu atoms. The slower decrease and higher values of the normalized fluorescence at higher angles demonstrate that the heating process has also resulted in a much broader depth distribution of the Cu atoms. This indiffusion of Cu is consistent with an estimated diffusion coefficient $D = 1.5 \times 10^{-11}\,\mathrm{cm}^2/\mathrm{s}$ for Cu in CdTe at 200 °C,[15] which leads to an additional diffusion of about 2000 nm in 1 h.

As shown in Fig. 2, the EXAFS χ function of the sample after heating appears quite different from that before heating. From detailed curve fitting, the first and second prominent peaks in the Fourier transforms have been identified as arising from Te neighbors around the Cu impurities in CdTe. Before second heating, the first Te neighboring shell has coordination numbers of 4.1 at a distance of 1.68 Å and the second Te neighbors are at 2.61 Å from Cu with a coordination number 2.7. As compared to the Cd–Te bond length of 2.81 Å in bulk CdTe,[16] the short distance 1.68 Å between Cu and the first Te neighboring shell shows that some Cu atoms do not substitute for the cation Cd sites in CdTe. A plausible suggestion for the location of these Cu impurities is that either they are at some interstitial sites or form small Cu–Te complexes around the Te atoms in the host CdTe, most pos-

TABLE I. Parameters of local structure around Cu obtained from curve fitting the Cu K-edge EXAFS. The amplitude reduction factor S_0^2 representing the central atom shake-up and shake-off effects and the mean free path of photoelectrons λ are determined from curve fitting the data of a pure Cu sample with coordination numbers and interatomic distances obtained from x-ray diffraction data.[a] N is the coordination number. R is the bond length. σ^2 is the Debye–Waller-like factor serving as a measure of local disorder. ΔE_0 is the difference between the zero kinetic energy value of the sample and that of the theoretical model used in FEFF.

Sample	Atom	N	R (Å)	σ^2 (10^{-3} Å^2)	ΔE_0 (eV)	λ (Å)	S_0^2
CdTe	Te (nn)	4.1	1.68	14	0.7	6.1	0.8
CdTe	Te (nnn)	2.7	2.61	11	0.9	6.1	0.8
CdTe heated	Te (nn)	2.3	1.68	23	−1.0	6.1	0.8
CdTe heated	Te (nnn)	1.7	2.65	10	4.5	6.1	0.8

sibly accompanied by a rather large local distortion of the CdTe unit cell. Since no other Cu near neighbors are found, it suggests that the Cu impurities do not form clusters by themselves; this is reasonable in light of the very low concentration of the dilute Cu impurity atoms in the material. On the other hand, the second peak in the Fourier transform indicates a Te near neighbor shell at 2.61 Å, this is most likely due to Cu substitution for the Cd sites but associated with some local lattice distortion. Although this Cu–Te bond length is shorter than the original Cd–Te bond in the host, this change is reasonable from the fact that the ionic radius of Cu is about 0.13 Å shorter than that of Cd in a tetrahedral bonding configuration and taking into account the experimental uncertainties (about 0.02 Å) in bond length determination. Further, this change in bond length is also consistent with a recent calculation by Wei *et al.* in which they predicted that the Cu–Te bond lengths are about 6.7% shorter than the Cd–Te bond lengths.[17] This translates to 2.62 Å for the Cu–Te bond in CdTe:Cu.

After the second heating, the coordination number of the first Te neighboring shell was reduced to 2.3 with an increased local disorder as indicated by an increase of the Debye–Waller factor σ^2 (see Table I), but the bond length remains unchanged at 1.68 Å. The coordination number of the second Te neighbors was reduced to 1.7 with a slight increase of the bond length to 2.65 Å. This result suggests that heating at a moderate temperature of ~200 °C has not caused any substantial changes in the location of Cu impurities except for a reduced effective coordination number of Te atoms around Cu, mainly caused by the presence of additional local disorder associated with a broader redistribution of the Cu impurities. The second Fourier transform peak only shows a decrease of coordination number from 2.3 to 1.7 while the bond length and local disorder seem to remain practically the same within our experimental uncertainties. This might suggest that heating could lead to a possible reduction of the substitutional Cu impurities as a result of a broader and deeper distribution of all the Cu atoms. Hence, the main effects of heating could be attributed to a decrease of the coordination numbers and/or an increase of local disorder while the Cu impurities are redistributed through a deeper and broader depth profile in the CdTe host. The EXAFS spectra shown in Fig. 2 have also been compared with those obtained with a Cu_2Te compound, and our EXAFS data cannot allow the presence of any Cu_2Te in the material either before or after heating. These results shall be used in the near future for a comparison with Cu-doped polycrystalline CdTe to investigate the effects arising from grain boundaries.

In conclusion, our studies have shown that using Cu-containing back contacts in CdTe heterojunction photovoltaic devices could result in a diffusion of Cu impurities into CdTe. The majority of Cu atoms could either form a thin layer of small Cu–Te complexes around the Te atoms or occupy some interstitial sites near the CdTe surface while other Cu impurities substitute for the Cd sites in the host. Diffusion of Cu can be enhanced by thermal agitation such as heating at moderate temperature. Heating results in a redistribution of the Cu atoms through a deeper and broader profile accompanied by some local structural changes. Structural changes include the possibilities of (i) decreased coordination number of Te near neighbors, (ii) increased local disorder, and (iii) decreased effective valency of the Cu ions. Diffusion and structural changes could be related to significant changes in the electronic and optical properties of CdTe, thereby leading to possible efficiency changes of the photovoltaic devices.

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